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OPTICAL STARK EFFECT IN THE TWO-PHOTON SPECTRUM OF NO

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ABSTRACT

A large optical Stark effect has been observed in the two-photon spectrum $X^2\Pi \rightarrow A^2\Sigma^+$ in NO. It is explained as a near-resonant process in which the upper state of the two-photon transition is perturbed by interactions with higher-lying electronic states coupled by the laser field. A theoretical analysis is presented along with coupling parameters determined from ab initio wave functions. The synthetic spectrum reproduces the major experimental features.

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In this letter, we are reporting a quantitative determination of the optical Stark effect in a molecular, two-photon, electronic transition. Optical Stark effects have previously been observed in resonant, two-photon, atomic transitions[1] and in resonant, multiphoton ionization of atoms.[2] Because of the high density of states, molecular Stark effects should be more easily observed, especially in multiphoton transitions using high laser intensities. In fact, such observations have been reported by Otis and Johnson[3] in the multiphoton ionization of NO; by Srinivisan et al.[4] in two- and three-photon resonant sum frequency mixing in H_2; and by Girard et al.[5] in the two-photon excitation of CO. However, to our knowledge, previous analyses of Stark effects in molecular multiphoton transitions have been limited to order-of-magnitude estimates.

Two of us[6,7] have developed a laser-induced fluorescence technique for temperature diagnostics in low-temperature gas flows seeded with low concentrations of NO. The method relies on the two-photon excitation of two selected, ro-vibronic transitions in the NO $\gamma(X^2\Pi,\ v'' = 0 \rightarrow A^2\Sigma^+,\ v' = 0)$ band. Because of the inherently weak two-photon interaction, high laser intensities are required to provide adequate signal levels. However, even at moderate power levels, unexpectedly large Stark broadening was observed in the spectrum. Therefore, we have studied the Stark effect in some detail to understand the nature of the broadening mechanism.

The experimental arrangement used was similar to that described in Ref. 7. Selected regions of the $\gamma(0,0)$, two-photon, fluorescence-excitation spectrum were scanned with a dye laser, which was pumped by a Nd:YAG laser operated at 10 Hz. A linearly polarized beam was generated

at wavelengths near 450 nm, with a 5-nsec pulse duration, an average linewidth of ≈0.2 to 0.3 cm^{-1}, and with energies of a few mJ. The beam intensity distribution was spatially and temporally nonuniform, and varied from pulse to pulse. A large fraction of the beam energy was focused into a sample cell for the Stark measurements. Approximately 10% was split off and loosely focused into a reference cell to provide a simultaneous spectrum with negligible Stark broadening. NO pressures were identical in both cells and ranged from 0.05 to 0.1 torr, where collisional broadening was negligible. The broadband fluorescence from each cell was collected at 90°, and then imaged onto a photomultiplier through an aperture that limited observation to a 1 mm path length at the focal point. Signals were integrated and averaged with a boxcar integrator.

An example of the broadening for a spectral region in which the line separations are significantly greater than the laser bandwidth is shown in Fig. 1. The upper trace was taken using an average laser intensity of ≈3 GW/cm^2. The lower trace, recorded simultaneously with a reduced laser power level, shows a spectrum where the Stark effect is negligible. The upper spectrum displays an asymmetric shift to the blue for both the $S_{11} + R_{21}(20\text{-}1/2)$ and $S_{21}(16\text{-}1/2)$ transitions. The rotational sublevels, which are split by the laser field, are not resolved. The splitting appears in the spectrum as a broadening, 3 to 4 cm^{-1} wide. Additionally, the relative heights of the two peaks are reversed. Figure 2 shows a plot of the full width at half maximum (FWHM), of the $S_{11} + R_{21}(20\text{-}1/2)$ and $S_{11} + R_{21}(7\text{-}1/2)$ lines, as a

function of the average laser energy. The width is linearly proportional to the pulse energy, indicating a quadratic Stark effect. The intercept at zero energy corresponds to the convoluted two-photon laser width and Doppler width.

To account for the observed Stark effect quantitatively, both shifts and widths induced by the optical field need to be considered. A survey of spectroscopic data for NO[8-13] shows that at the laser frequencies for the two-photon $X \rightarrow A$ transition, each rotational level of the A state is near-resonant with a one-photon transition from a J level of a high-lying discrete electronic state. The observed splitting can be attributed to near-resonant, one-photon coupling via the Stark field (i.e., a quadratic Stark effect). In addition to the splitting, a significant width is also introduced since the A state can be coupled with the ionization continuum by two-photon transitions, which are enhanced by the near-resonant one-photon step. This additional width corresponds to a quartic Stark effect.

An important factor in determining the magnitude of the observed Stark effect is the resonance-energy gap, G (the difference between the energies of the perturbing state and the sum of the A state and photon energies). From the experimental data in the region near one-photon resonance (≈450 nm) with the A state,[8-13] the strongest perturbing level of the $S_{11} + R_{21}(20\text{-}1/2)$ branch has been identified as: $B^2\pi$, v = 25; and for the $S_{21}(16\text{-}1/2)$ branch, $K^2\pi$, v = 1. The zero-field resonance-energy gaps were calculated with expressions appropriate for intermediate coupling between Hund's case (a) and (b).[14] The results are given in Table I. The spectroscopic parameters used were derived from experimental data.[11,13,15] In particular, the rotational constants, B_J, used for

the $^2\Pi$ states were consistent with the recent work of Ebata et al.[11] Since the smallest gap is less than 5 cm^{-1} for all three A-state rotational levels considered, large Stark shifts are observed.

We have calculated the Stark shifts in NO by solving the time-dependent Schrödinger equation directly. The commonly used perturbation approach[5] was found to be inadequate, owing to the small resonance-energy gaps. Calculations were performed for the combined molecule and field system with the A state coupled to six rotational levels of the $B^2\Pi$ or $K^2\Pi$ state, via dipole interactions; i.e., $J = J_A + 1, J_A, J_A - 1$ for each of the spin components, F_1 and F_2, of the perturbing state. Contributions from the $X^2\Pi$ state have been neglected because they are small. In the restricted part of the Hilbert space, consisting of bound molecular eigenstates, resonantly or near-resonantly coupled, and with their natural lifetimes neglected (dressed molecule representation[16]), we can cast the Schrödinger equation into the form of a secular equation.[17] For a state A, coupled to a set of bound states I and J, through the potential V, we have[18]

$$\vec{G} + \vec{V} - \vec{\alpha} = 0 \tag{1}$$

where $G_{AA} = 0$, $G_{IJ} = (E_I - E_A - \omega)\delta_{IJ}$, $V_{AA} = 0$, and

$$V_{AI} = -\frac{1}{2}\,\varepsilon\,\mu_{AI}\,R(J_A, J_I, S_A, S_I, M) \tag{2}$$

Also, we set $V_{IJ} = 0$, because in the present case these terms are nonresonant. In Eq. (2), μ_{AI} is the transition dipole moment, R is a rotational line shift factor, and ε is the field strength. Associated

with each eigenvalue, α_N, there is a dressed state wave function, $\Psi_N(\vec{r},t)$, given by

$$\Psi_N(\vec{r}, t) = \left[B_{NA}(\Phi_A, n) + \sum_I B_{NI}(\Phi_I, n-1)\right] e^{-i\left[E_A + \left(n + \frac{1}{2}\right)\omega - \alpha_N\right]t}, \quad (3)$$

where Φ_A and Φ_I are the time-independent molecular eigenfunctions; B_{NA} and B_{NI} are time-independent coefficients; and n, $n-1$ are photon number states. The wave function, $\Psi(\vec{r}, t)$, which satisfies the boundary condition that $\Psi(\vec{r}, 0) = (\Phi_A, n)$, is a linear combination of the Ψ_N's according to

$$\Psi(\vec{r}, t) = \sum_N C_N \psi_N(\vec{r}, t). \quad (4)$$

The wavefunction is nonstationary and oscillates among the Ψ_N's, depending on time. For the case of two-state coupling (Autler-Townes effect[19]), our result agrees with that obtained previously in closed form.[20]

While $\Psi(\vec{r}, t)$ is oscillatory, the laser probes only one of its components. Since a single laser field was used in this experiment, the probe and Stark fields are identical, and are always tuned to the component of $\Psi(\vec{r}, t)$ with α closest to zero. We designate it as Ψ_0. The eigenvalue, α_0, then corresponds to the Stark shift observed. To determine α_0, Eq. (1) is solved separately for each M level. The parameters used in the calculation are the resonance-energy gap, G, and the coupling potential, V. Since the experiment requires the Stark and probe frequencies to be equal, Eq. (1) is solved iteratively until the two frequencies agree.

The determination of the rotational line shift factor, R, depends on the Hund's coupling case for which the pair of molecular eigenstates, A and I, belong. Assuming the use of a single, linearly polarized laser, for the general case of intermediate coupling between Hund's case (a) and (b), we find that

$$R(J_A, J_I, S_A, S_I, M) = \left(\frac{2J_A + 1}{2J_I + 1}\right)^{1/2} C(J_A 1 J_I, MOM)$$

$$\times \left[\sum_{\Omega_A=-1/2}^{1/2} \sum_{\Omega_I=1/2}^{3/2} < A^2\Sigma^+, J_A \pm \frac{1}{2} | A^2\Sigma^+, \Omega_A > \right.$$

$$\left. \times C(J_A 1 J_I, \Omega_A 1 \Omega_I) < {}^2\Pi, J_I \pm \frac{1}{2} | {}^2\Pi, \Omega_I > \right]. \quad (5)$$

Here Rose's definition of Clebsch-Gordan coefficients are used.[21]

The two-photon rotational line strength, $S(J_X, J_A, S_X, S_A, M)$, between individual M levels of the $X^2\Pi$ and $A^2\Sigma^+$ states, determines the shape of the Stark spectrum. The M-dependent line strength can be deduced from the unresolved two-photon rotational line strength of Halpern et al.,[22] (valid for intermediate coupling) and is given by

$$S(J_X, J_A, S_X, S_A, M) = \frac{5|C(J_A 2 J_X, MOM)|^2}{2J_X + 1} S(J_X, J_A, S_X, S_A). \quad (6)$$

The Stark width is introduced by the interaction of the wavefunction, Ψ_0, with the ionization continuum via the radiation field and is expressed by

$$\Delta\Gamma = \frac{\pi}{2} \sum_{\lambda} | < \Phi_{c,\lambda} | \vec{\mu} \cdot \vec{\varepsilon} | \Psi_0 > |^2 . \qquad (7)$$

The continuum states are evaluated at energy, $E_C = E_A + 2\omega$, and the subscript, λ, sums over all degenerate quantum numbers. The Stark width, $\Delta\Gamma$, is also M-dependent through rotational factors similar to R. The energy shift, due to coupling to the continuum, is found to be numerically small for NO and will not be considered.

The vibronic transition moments, μ_{AI}, necessary to evaluate the Stark effects have been calculated using ab initio wave functions. The electronic wave functions were calculated using a large (32σ, 22π, 6σ, 4ϕ), Slater-type basis set containing Rydberg functions.[17] Complete-Active-Space SCF calculations[25] (CASSCF) were carried out for the $A^2\Sigma^+$ state, followed by multireference, first-order, configuration-interaction (CI) calculations[24] for both $^2\Sigma$ and $^2\Pi$ symmetries.[25] Transition moments between the B,K states and the ionization continuum were calculated from discretized CI wavefunctions, using the Stieltjes imaging methods.[26]

The Stark shifts and widths of the three rotational levels of the $A^2\Sigma^+$ state have been calculated for the experimental field density, I_{AV}, of 3 GW/cm^2, using a chaotic field model for the photon statistical behavior.[27] Their values are shown in Table II for representative M levels. Both the shifts and widths are strongly M-dependent owing to a dominant M^2-dependent term in the rotational line shift factor. Uncertainties in energy gaps, transition moments, and I_{AV} contribute to the error in the theoretical Stark parameters. Since the rotational constants used in the calculation of G are not well known experimentally,

they constitute a major source of uncertainty. Because of the small energy gaps and the high J levels considered, a 1% variation in B_J introduces 20 to 40% changes in the Stark parameters. The errors associated with ab initio transition moments are difficult to determine. The calculated f number of the $X \rightarrow A$ (0,0) band, though, agrees with experiment to 5%,[17] indicating that the bound-bound transition moments should be reliable. The bound-free transition moments are subject to much larger errors, resulting in calculated widths that are less reliable than the shifts. The estimated uncertainty in I_{AV} is approximately 50%. Also, the nonuniformity in the beam intensity may change the calculated parameters to some extent.

A synthetic, Stark-broadened, two-photon spectrum of NO has been generated using the calculated parameters and is presented in Fig. 3. At a given probe frequency in the synthetic spectrum, all transitions that contributed to the intensity were convoluted with the laser and Doppler widths, using a Voigt function. The laser width was assumed to be composed of both probe and Stark fields, with an effective, single, Gaussian width of 0.5 cm^{-1}. The vertical lines in Fig. 3 represent the calculated positions of the Stark-shifted M level transitions at I_{AV}. The experimental spectrum taken at the same field strength is also reproduced in the figure. Comparing the two spectra, we find overall agreement. Both spectra show asymmetric shifts to the blue and a peak-height reversal from the weak-field case. The asymmetry is the result of M-dependent blue shifts and the intensity distributions of the shifted lines. The individual Stark widths smooth the line shape. Nevertheless,

there are some discrepancies. On the high-frequency side of the $S_{11} + R_{21}(20\text{-}1/2)$ transition, the synthetic spectrum is more intense. Also, the calculated $S_{12}(16\text{-}1/2)$ transition is narrower than observed. These differences are probably due to uncertainties in the data used to determine the Stark parameters. We have varied B_J and I_{AV} over a reasonable range of uncertainty and found that the major features of the spectrum were insensitive. Only the shape of the spectrum for large M transitions showed minor changes.

In conclusion, a theoretical method has been developed that should be uniquely applicable to near-resonant Stark effects. Several aspects of the model were found to be essential for reproducing the experimental features in NO. In particular, the time-dependent Schrödinger equation had to be solved directly since perturbation methods were unsuccessful. Additionally, an iterative solution of the secular equation was necessary to account for the single beam experiment properly.

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TABLE I. Energy gap G_{AI} in cm^{-1} used in the calculation of Stark parameters[i]

Perturbing $^2\pi$ state	$A^2\Sigma^+$, v = 0		
	(a) F_1, J_A = 22-1/2	(b) F_2, J_A = 21-1/2	(c) F_2, J_A = 18-1/2
F_1, $J = J_A + 1$	54.3	-4.2	-28.5
F_1, $J = J_A$	-4.2	-60.2	-85.5
F_1, $J = J_A - 1$	-60.2	-113.6	-139.5
F_2, $J = J_A + 1$	71.3	17.6	57.7
F_2, $J = J_A$	17.6	-33.9	-2.9
F_2, $J = J_A - 1$	-33.9	-83.2	-60.5

[i]For columns a and b, the perturbing $^2\pi$ state is $B^2\pi$, v = 25. For column c, it is $K^2\pi$, v = 1.

TABLE II. Stark shifts (cm^{-1}) and widths (cm^{-1}) calculated for three rotational levels of the $A^2\Sigma^+$, v = 0 state at I_{AV} = 3 GW/cm^2

	F_1, J = 22-1/2		F_2, J = 21-1/2		F_2, J = 18-1/2	
M	Shift	Width	Shift	Width	Shift	Width
1/2	-0.03	0.06	-0.41	0.39	-0.02	0.04
5-1/2	0.99	0.42	-0.25	0.35	1.02	0.70
10-1/2	2.44	0.52	0.22	0.27	2.41	0.91
15-1/2	3.83	0.49	1.11	0.21	3.87	0.93
20-1/2	5.03	0.46	2.53	0.20	--	--

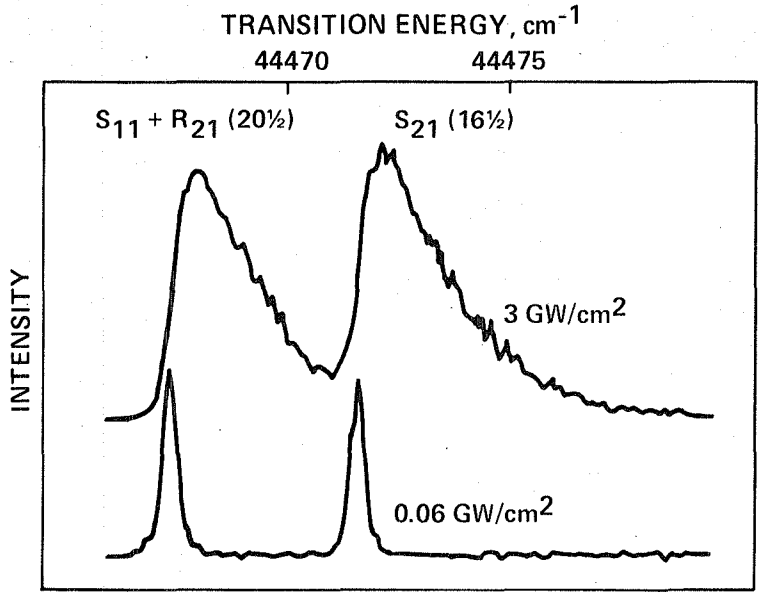

Figure 1.- Experimental two-photon spectrum of NO, $X^2\Pi$, v" = 0 → $A^2\Sigma^+$, v' = 0, $S_{11} + R_{21}(20\text{-}1/2)$, and $S_{21}(16\text{-}1/2)$ transitions. The upper trace (high field) was taken using 2-mJ pulse energy and a focused beam diameter ≈100 to 150 μ. The corresponding parameters for the lower trace are 0.2-mJ energy and ≈300-μ diameter. NO pressure was 0.1 torr in both cases.

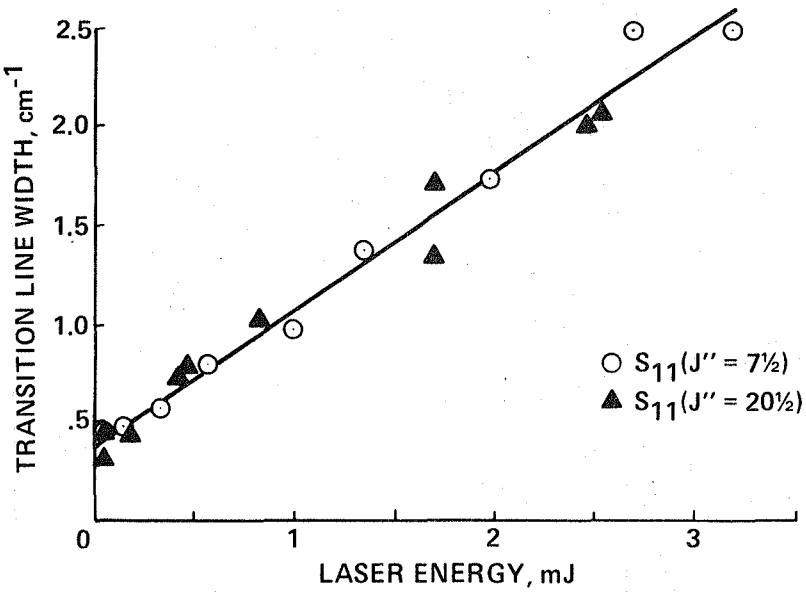

Figure 2.- Linewidth (FWHM) of the $S_{11} + R_{21}(20\text{-}1/2)$ and $S_{11} + R_{21}(7\text{-}1/2)$ lines as a function of laser energy. Focused beam diameter was ≈300 μ. NO pressure was 0.05 torr.

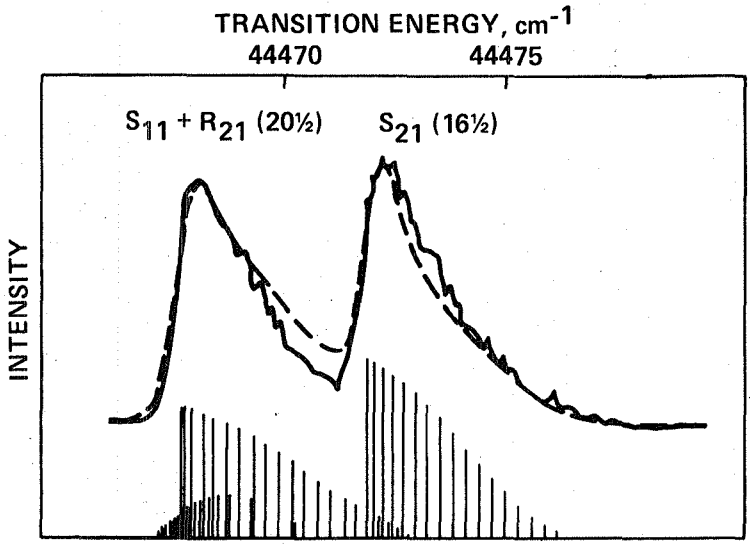

Figure 3.- Comparison of the synthetic (---) and experimental (——) high-field spectra of the transitions shown in Fig. 1. The vertical lines represent the calculated positions of the shifted M levels.

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16. Abstract

A large optical Stark effect has been observed in the two-photon spectrum $X^2\Pi \rightarrow A^2\Sigma^+$ in NO. It is explained as a near-resonant process in which the upper state of the two-photon transition is perturbed by interactions with higher-lying electronic states coupled by the laser field. A theoretical analysis is presented along with coupling parameters determined from ab initio wave functions. The synthetic spectrum reproduces the major experimental features.

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